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CLARIFICATION OF GLASS USING ARSENIC AND ANTIMONY OXIDES

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The capacity of melted glasses of different compositions for being clarified by arsenic and antimony oxides is analyzed taking examples of industrial silicate optical crowns. It is established that the kinetics of the reaction of decomposition of arsenic pentoxide responsible for removing bubbles from the glass melt is closely related to the redox potential of the melt. Practical recommendations are given.

Small additives of arsenic and antimony oxides are successfully used as clarifiers and chemical decolorizing agents in glass melting practice. Clarification of glass melt is implemented as a consequence of the following reactions [1]:

$$(Me)_n(NO_3)_m \Rightarrow Me_nO_m + NO_2 + O_2; \quad (1)$$

$$[As(Sb)]_2O_3 + O_2 \Rightarrow [As(Sb)]_2O_5; \quad (2)$$

$$[As(Sb)]_2O_5 \Rightarrow [As(Sb)]_2O_3 + O_2. \quad (3)$$

Nitrate is an obligatory component of arsenic- and (or) antimony-bearing batches; in decomposing according to reaction (1) it releases oxygen, which at the charging temperature is absorbed by arsenic oxide (III) according to reaction (2), A further increase in temperature in the course of clarification initiates process (3) responsible for removing glass melt from bubbles.

At first glance the quality of clarification depends on the quantity of arsenic and (or) antimony oxide, the content of salpeter in the batch, and the melt viscosity. However, in practice this is not quite so. Viscous high-silica crowns are often better clarified than, for instance, heavy crowns melted at a lower temperature. The purpose of this study is to investigate the capacity of glasses of various compositions for being clarified by arsenic and antimony oxides.

We investigated 18 clear industrially produced optical silicate glasses including light crowns (LC), crowns, barite crowns (BC), and heavy crowns (HC). The content of bivalent ion $d_{Fe(II)}$ and the basicity coefficient K_{bas} were determined for each glass. The content of bivalent iron is an indicator of the degree of basicity of the glass [2] controlling the redox potential of the total glass melt, i.e., it takes into account the simultaneous effect of several factors: oxide composition of glass, time-temperature and redox conditions of melting and batch composition. It is known, for instance, that formation of Fe(II) is facilitated by an increased content of acid oxides (SiO_2, B_2O_3, Al_2O_3), increased temperature, melting duration, and the amount of reducing components and carbonates in the batch [3, 4]. The basicity coefficient takes into account only the oxide content of glass [5]. The value K_{bas} was calculated from the following expression [5]:

$$K_{bas} = [4.6Al_2O_3 + 4.7(K_2O + Na_2O + BaO + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)] \times \{0.82SiO_2 + [B_2O_3 - (K_2O + Na_2O + BaO + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)]\}^{-1},$$

where the coefficients in front of the oxides express their molar content, %.

The calculation results are given in Table 1, which also lists the total molar content of the clarifying agents and the best possible class of bubbles for glass of a particular grade. The number of bubbles per 1 kg of consecutively glass grows from class A to class E.

Clarification of glass melt using arsenic or antimony oxides is implemented by means of consecutive reactions (1) – (3). Process (3) is directly responsible for clarification, i.e., for removing bubbles that have reached an optimum size and sufficient buoyancy from the glass melt. Therefore, the efficiency of clarification to a large extent is determined by the completeness and case of decomposition of arsenic (antimony) pentoxide delivering oxygen to gas inclusions penetrating the glass melt. The kinetics of reaction (3) ought to be closely related to glass basicity, since variable-valence elements in acid compositions tend to retain the lowest degree of oxidation, whereas in base compositions they tend to retain the highest degree of oxidation. Accordingly, an increasing K_{bas} will delay reaction (3) and impede clarification of the glass melt. As a consequence, one can expect an increased number of bubbles in glass. In order to decrease it, it is probably necessary to increase the quantity of oxygen in-

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TABLE 1

Glass grade	Mass content of clarifiers, %		$d_{Fe(II)}$, %	K_{bas}	Bubble class, according to GOST 3514–78
	$As_2O_3 + Sb_2O_3$	including Sb_2O_3			
LK4	0.08	–	2.1	0.559	A
LK7	0.16	–	0.4	0.34	A
K2	0.08	–	1.5	0.843	A
K8	0.12	–	4.6	1.378	A
K14	0.12	–	2.7	1.263	A
K18	0.12	–	0.9	1.176	A
K19	0.13	–	3.6	1.606	A
BK4	0.18	–	3.5	2.010	A
BK6	0.18	–	6.1	2.510	A
BK8	0.18	–	3.8	1.630	B
BK13	0.28	0.08	6.9	2.200	B
TK1	0.14	0.07	5.6	2.220	B
TK4	0.42	0.15	7.2	4.310	C
TK12	0.17	0.05	5.5	2.100	C
TK13	0.09	0.09	7.6	3.160	B
TK14	0.28	0.05	7.1	3.760	E
TK20	0.10	0.10	7.9	5.740	D
TK21	0.25	0.16	6.6	14.590	D

TABLE 2

Glass grade	Total molar content of clarifiers, %	$d_{Fe(II)}$, %	K_{bas}	Bubble class
TK13	0.09	7.6	3.16	B
TK20	0.10	7.9	5.74	D
K19	0.13	3.6	1.61	A
TK1	0.14	5.6	2.22	B
BK13	0.23	6.9	2.20	B
TK21	0.25	6.6	14.58	D
LK7	0.16	0.4	0.34	A
TK21	0.17	5.5	2.10	C
TK1	0.14	5.6	2.22	B
K19	0.13	3.6	1.61	A

troduced into the system, i.e., to increase the content of the clarifiers in the batch composition. Table 2 compares the basicity coefficients and classes of bubbles in glasses of different grades having similar contents of clarifiers.

It can be seen that acid glasses with a low basicity coefficient have less bubbles among glasses with a similar concentration of clarifiers, i.e., with virtually equal quantity of oxygen that is formed in the system according to reaction (3). This corroborates the assumption that process (3) in alkali glasses is impeded and, accordingly, clarification is impaired.

The variable-valence elements present in glass interact according to the following redox series [1]:

$$CrO_3 \Leftrightarrow Mn_2O_3 \Leftrightarrow CeO_2 \Leftrightarrow CuO \Leftrightarrow As_2O_5 \Leftrightarrow Sb_2O_5 \Leftrightarrow Fe_2O_3;$$

$$Cr_2O_3 \Leftrightarrow MnO \Leftrightarrow Ce_2O_3 \Leftrightarrow Cu_2O \Leftrightarrow As_2O_3 \Leftrightarrow Sb_2O_3 \Leftrightarrow FeO.$$

Each left-standing oxide of the upper series in a higher valence state is capable of oxidizing any right-standing oxide of the lower series existing in a lower valence state. Therefore, the following reaction is possible between iron and arsenic (antimony):

$$As_2O_5 + FeO \Rightarrow As_2O_3 + Fe_2O_3.$$

This means that the content of Fe(II) is proportional to the content of As(V) in the glass melt. Since the content of bivalent iron and, accordingly, of pentavalent arsenic is higher in more alkaline glasses (Table 2), this corroborated the conclusion of the effect of glass composition on the process kinetics (3) determining the degree of clarification of the glass melt.

Table 3 shows the molar content of components and the amount of oxygen contained in 100 g of glass. The data are taken from [6]. The authors believe that dissolution of oxygen in glass is accompanied by its chemical interaction with variable-valence elements, including arsenic according to reaction (2).

A simple calculation of the quantity of oxygen based on Eq. (2) and correlating these results with experimental data (Table 3) make it possible to estimate the part of As(V) in glass. This content is obviously higher in alkali glasses; therefore, the equilibrium As(V) $\Leftrightarrow$ As(III) is shifted to the left. This makes it possible to interpret the data in Table 1 in the context of acid-base relations.

Table 4 was constructed for a better presentation, in which the glasses investigated are split into 6 groups with increasing K_{bas} values.

It can be seen that the number of grades with the least number of bubbles (class A) consecutively decreases from 100 to 40% as K_{bas} grows to 3. A further increase in K_{bas} increases the number of bubbles (to class B or lower). The content of bivalent iron and the glass basicity coefficient grow symbatically passing from the first to the sixth group. The content of Fe(II) and the clarifiers generally obeys the same dependence. This regularity is not satisfied only in group 6, despite a decreased content of clarifiers. The content of

TABLE 3

Sample	Molar content, %					Content of oxygen, ml per 100 g glass	K_{bas}	$d_{As(V)}$, %
	SiO_2	As_2O_3	PbO	K_2O	Na_2O			
1	63.20	0.26	30.90	2.96	2.69	13.47	5.21	26.5
2	71.07	0.15	19.64	6.95	2.19	3.60	3.04	10.6

TABLE 4

Glass group	K_{bas}	Mean values, %		Number of glass grades with bubble class, %					Total number of glass grades in group
		of Fe(II) part	of molar content of clarifiers	A	B	C	D	E	
1	< 1.0	1.3	0.11	100	–	–	–	–	3
2	1.0 – 1.5	2.7	0.12	66	34	–	–	–	3
3	1.5 – 2.0	3.7	0.16	50	–	50	–	–	2
4	2.0 – 3.0	5.5	0.19	40	40	10	–	–	5
5	3.0 – 5.0	6.3	0.26	–	33	33	–	34	3
6	> 5.0	7.2	0.18	–	–	–	100	–	2

Fe(II) increases, probably due to the intense reducing effect of glass batches TK20 and TK21, which contain the highest amount of mono- and bivalent metal oxides, since these oxides are usually introduced via carbonates that have a reducing effect on iron [7].

Thus, the kinetics of the reaction of decomposition of arsenic pentoxide responsible for the removal of bubbles from the glass melt is closely related to the redox potential of the melt. In alkali glasses, this reaction is delayed, which leads to a higher degree of bubbles.

In optical glass melting practice in order to increase the amount of oxygen penetrating into the melt in the decomposition of $[As(Sb)]_2O_5$ and improve clarification of alkali glasses, one should introduce increased quantities of arsenic (antimony) oxides, i.e., proportionally to the coefficient of glass melt basicity.

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